

AD-A241 333



DTIC

(2)

SECT

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT Approval for public release; distribution unlimited	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. DU/DC/TR-24		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry Duke University	6b. OFFICE SYMBOL (if applicable)	7b. ADDRESS (City, State, and ZIP Code) 300 North Quincy Street Arlington, VA 22217-5000	
6c. ADDRESS (City, State, and ZIP Code) Durham, NC 27706		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-89-J-1545; R&T Code 4135008	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable)	10. SOURCE OF FUNDING NUMBERS	
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		PROGRAM ELEMENT NO. NR	PROJECT NO. 053
		TASK NO. 841	WORK UNIT ACCESSION NO.
11. TITLE (include Security Classification) ON THE SYNTHESIS AND CHARACTERIZATION OF NOVEL ALUMINUM-ARSENIC COMPOUNDS; CRYSTAL STRUCTURE OF $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$			
12. PERSONAL AUTHOR(S) L. Wells, A.T. McPhail, and T. M. Speer			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) 1991-10-03	15. PAGE COUNT 18
16. SUPPLEMENTARY NOTATION Accepted for publication in <u>Organometallics</u> .			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		aluminum-arsenic, synthesis, crystal structure, ring compound	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) See attached.			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Richard L. Wells		22b. TELEPHONE (Include Area Code) 22c. OFFICE SYMBOL (919)660-1541	

91-12706



[19. ABSTRACT]

**On the Synthesis and Characterization of Novel
Aluminum-Arsenic Compounds;
Crystal Structure of $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$.**

Richard L. Wells*, Andrew T. McPhail and Timothy M. Speer

Department of Chemistry, Paul M. Gross Chemical Laboratory

Duke University, Durham NC, 27706

(Received, 1991)

ABSTRACT

The viability of dehalosilylation and lithium chloride elimination reactions for use in the preparation of compounds containing core rings of the type $\overline{\text{Al-As-Al-As}}$ and $\overline{\text{Al-As-Al-Cl}}$ was investigated. The second fully characterized aluminum-arsenic dimer, $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$ (**1**), was isolated from a coupling reaction between Et_2AlCl and $\text{LiAs}(\text{SiMe}_3)_3$ carried out at -78°C . Dehalosilylation reactions between Et_2AlCl and $\text{As}(\text{SiMe}_3)_3$ in 1:1 and 2:1 mole ratios at ambient temperature failed to give the expected products, instead yielding the adduct $\text{Et}_2(\text{Cl})\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$ (**2**). As evidenced by ^1H NMR spectra, an NMR tube sample of **2** in benzene- d_6 did undergo internal dehalosilylation to give **1** when heated to 87°C in an oil bath. X-ray crystallographic analysis of **1** confirms its dimeric solid-state structure and shows the $\overline{\text{Al-As-Al-As}}$ ring to be planar. Compound **1** crystallizes in the monoclinic system, space group $C2/c$ (C_{2h}^6), with four molecules in a unit cell of dimensions: $a = 18.214(2) \text{ \AA}$, $b = 9.542(1) \text{ \AA}$, $c = 20.453(2) \text{ \AA}$, $\beta = 99.89(1)^\circ$.



Accession for
NTIS GPOAL
DTIC TAB
Unannounced
Justification

By
Distribution

Availability

Dist

A-1

OFFICE OF NAVAL RESEARCH

Grant NOOO14-89-J-1545

R&T Code 4135008

Technical Report No. DU/DC/TR-24

ON THE SYNTHESIS AND CHARACTERIZATION OF NOVEL ALUMINUM-ARSENIC
COMPOUNDS; CRYSTAL STRUCTURE OF $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$

by

R. L. Wells, A. T. McPhail, and T. M. Speer

Prepared for Publication in Organometallics

Duke University
Department of Chemistry
Durham, NC 27706

October 3, 1991

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

[Submitted to *Organometallics*, August 21, 1991]

**On the Synthesis and Characterization of Novel
Aluminum-Arsenic Compounds;
Crystal Structure of $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$.**

Richard L. Wells*, Andrew T. McPhail and Timothy M. Speer

*Department of Chemistry, Paul M. Gross Chemical Laboratory
Duke University, Durham NC, 27706*

(Received, 1991)

The viability of dehalosilylation and lithium chloride elimination reactions for use in the preparation of compounds containing core rings of the type $\overline{\text{Al-As-Al-As}}$ and $\overline{\text{Al-As-Al-Cl}}$ was investigated. The second fully characterized aluminum-arsenic dimer $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$ (**1**), was isolated from a coupling reaction between Et_2AlCl and $\text{LiAs}(\text{SiMe}_3)_3$ carried out at $-78\text{ }^\circ\text{C}$. Reactions between Et_2AlCl and $\text{As}(\text{SiMe}_3)_3$ in 1:1 and 2:1 mole ratios at ambient temperature failed to give the expected dehalosilylation products, instead yielding the adduct $\text{Et}_2(\text{Cl})\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$ (**2**). As evidenced by ^1H NMR spectra, an NMR tube sample of **2** in benzene- d_6 did undergo internal dehalosilylation to give **1** when heated to $87\text{ }^\circ\text{C}$ in an oil bath. X-ray crystallographic analysis of **1** confirms its dimeric solid-state structure and shows the $\overline{\text{Al-As-Al-As}}$ ring to be planar. Compound **1** crystallizes in the monoclinic system, space group $C2/c$ (C_{2h}^6), with four molecules in a unit

cell of dimensions: $a = 18.214(2) \text{ \AA}$, $b = 9.542(1) \text{ \AA}$, $c = 20.453(2) \text{ \AA}$, $\beta = 99.89(1)^\circ$.

INTRODUCTION

Of late, there has been heightened interest in the preparation of compounds that may serve as single-source precursors to Group 13-15 semiconductor materials.^{1,2} Two methods have been developed in our laboratories to fabricate compounds that may prove useful to this end: a) dehalosilylation between tris(trimethylsilyl)arsine and a Group 13 halide and b) coupling reactions involving lithium bis(trimethylsilyl)arsenide and a Group 13 halide. These methodologies have been applied to systems involving the heavier Group 13 elements to prepare compounds with core rings of the type $\overline{\text{M-As-M-As}}$ and $\overline{\text{M-As-M-Cl}}$, where $\text{M} = \text{Ga}$ and In .³⁻⁷ In an attempt to utilize these tactics to prepare analogous aluminum-arsenic species, reaction of Et_2AlCl with tris(trimethylsilyl)arsine and lithium bis(trimethylsilyl)arsenide was undertaken. While proving useful in the cases of Ga and In, room temperature dehalosilylation reactions failed in this work instead yielding the adduct $\text{Et}_2(\text{Cl})\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$ (**2**). The novel dimer $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$ (**1**), was prepared by a coupling reaction and is only the second Al-As dimer fully characterized by single crystal X-ray analysis.

EXPERIMENTAL

General Considerations. All reactions and manipulations were carried out utilizing standard Schlenk techniques, under an Ar atmosphere in a Vacuum/Atmospheres HE-43 Dri-Lab or under vacuum. Pentane and hexane were dried over LiAlH_4 while all other solvents were dried over, and distilled from, sodium benzophenone ketyl. Tris(trimethylsilyl)arsine and lithium bis(trimethylsilyl)arsenide

were prepared by the methods of Becker *et al.*⁸ Diethylaluminum chloride was purchased from Strem Chemicals, Inc. and used without further purification. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{27}\text{Al}\{^1\text{H}\}$ NMR spectra were obtained at 299.943, 75.4 and 78.2 MHz, respectively, on a Varian XL-300 spectrometer in 5 mm tubes. $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra were referenced to TMS using the carbons or residual protons of benzene- d_6 at δ 128 ppm and δ 7.15 ppm, respectively. $^{27}\text{Al}\{^1\text{H}\}$ spectra were referenced externally to $\text{Al}(\text{NO}_3)_3$ at δ 0.00 ppm. All spectra were run in benzene- d_6 and NMR tubes were flame sealed under vacuum. Melting points were obtained on a Hoover Uni-Melt in sealed capillaries and are uncorrected. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. Crystals used in X-ray analyses were flame sealed under argon in 0.7 mm thin-walled glass capillaries. Volatile reaction products were analyzed for Me_3SiCl content by hydrolysis with deionized water followed by titration of the resulting HCl solution with standard NaOH to a phenolphthalein endpoint. NaOH was standardized against potassium hydrogen phthalate to a phenolphthalein endpoint.

Preparation of $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$ (1). $\text{LiAs}(\text{SiMe}_3)_2$ (0.373 g, 1.63 mmol) was dissolved in 25 mL of pentane and 10 mL of THF in the top bulb of a two-bulb reaction flask. Et_2AlCl (0.1969 g, 1.633 mmol) was washed into the bottom bulb with 35 mL pentane. The lower bulb was cooled to $-78\text{ }^\circ\text{C}$ in an acetone/dry ice bath and the upper bulb was cooled with a liquid nitrogen wand. Upon mixing, a white precipitate formed (presumably LiCl , 0.0588 g, 87% yield) and the solution remained clear. After stirring for 18 h at $-78\text{ }^\circ\text{C}$, the reaction mixture was allowed to warm slowly to room temperature and volatiles were removed *in vacuo* to leave an off-white semi-solid that was recrystallized at $-15\text{ }^\circ\text{C}$ from pentane to give **1** (0.651 g, 65.2% yield), mp $201\text{ }^\circ\text{C}$. No Me_3SiCl was eliminated over the course of the reaction. Anal. Calcd. (found) for $\text{C}_{20}\text{H}_{56}\text{Al}_2\text{As}_2\text{Si}_4$: C 39.20 (39.40), H 9.15 (9.16). ^1H NMR: δ 0.42

[s, Si(CH₃)₃, 18H], 0.51 (q, CH₂, 4H) 1.38 (t, CH₃, 6H). ¹³C{¹H} NMR: δ 4.65 [s, Si(CH₃)₃], 9.68 (s, CH₃), CH₂ not observed. ²⁷Al{¹H} NMR: δ 181.87 (br s).

Preparation of Et₂(Cl)Al•As(SiMe₃)₃ (2). (a) **Reaction of Et₂AlCl with As(SiMe₃)₃ (1:1 mole ratio).** Et₂AlCl (0.2058 g, 1.670 mmol) in 25 mL of pentane was added to As(SiMe₃)₃ (0.492 g, 1.67 mmol) in 25 mL of pentane in a one-necked, round-bottomed flask equipped with a magnetic stir bar and fitted with a Teflon valve. No color change or precipitate formation was noted upon mixing. Following stirring at room temperature for 3 d, volatiles were removed *in vacuo* leaving an off-white solid that was recrystallized from pentane at -15 °C to give **2** (0.684 g, 98.7% yield), mp 138 °C. No Me₃SiCl was eliminated over the course of the reaction. Anal. Calcd. (Found) for C₁₃H₃₇AlAsClSi₃: C 37.62 (37.37), H 8.99 (8.89), Cl 8.54 (8.12). ¹H NMR: δ 0.28 [s, Si(CH₃)₃, 27 H], 0.46 (q, CH₂, 4H), 1.52 (t, CH₃, 6H). ¹³C{¹H} NMR: δ 3.09 (s, Si(CH₃)₃), 9.77 (s, CH₃), CH₂ not observed. ²⁷Al{¹H} NMR: δ 165.32 (br s). (b) **Reaction of Et₂AlCl with As(SiMe₃)₃ (2:1 mole ratio).** Et₂AlCl (0.3934 g, 3.20 mmol) in 20 mL pentane was added to As(SiMe₃)₃ (0.470 g, 1.60 mmol) in 30 mL pentane in a one-necked, round-bottomed flask equipped with a magnetic stir bar and fitted with a Teflon valve. No color change or precipitate formation was seen upon addition. Following stirring for 3 d at room temperature, volatiles were removed *in vacuo* to leave an off-white solid which was recrystallized from pentane at -15 °C to give clear crystals (0.653 g 98.3% yield), mp and NMR spectra (¹H and ¹³C{¹H}) match those of an authentic sample of **2**, *vide supra*. No Me₃SiCl was eliminated over the course of the reaction.

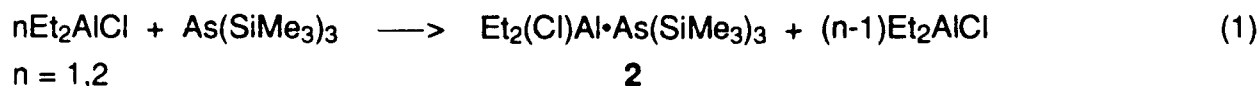
Intramolecular Dehalosilylation of 2 to Form 1. An NMR tube sample of **2** in benzene-d₆ was heated to 87 °C in an oil bath for 4 d. ¹H NMR spectra taken over this time showed peaks consistent with an authentic sample of **1** and one that may be attributed to Me₃SiCl at δ 0.165, indicating that internal dehalosilylation occurred.

Attempted Conversion of 1 to $\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2\text{Al}(\text{Et})_2\text{Cl}$. Et_2AlCl (0.0376 g, 0.312 mmol) in 20 mL of pentane was added to **1** (0.0956 g, 0.156 mmol) in a one-necked, round-bottomed flask fitted with a Teflon valve and equipped with a magnetic stir bar. Following stirring for 2 d at room temperature, volatiles were removed *in vacuo* to leave an off white semi-solid that was recrystallized from pentane at -15 °C, mp and NMR spectra (its ^1H and $^{13}\text{C}\{^1\text{H}\}$) matched those of an authentic sample of **1**, *vide supra*, indicating no reaction had occurred.

X-Ray Crystal Structure Analysis of 1. Crystallographic data are summarized in Table I. Intensity data were corrected for the usual Lorentz and polarization effects. An empirical absorption correction, based on the ϕ -dependency of the intensities of several reflections with ψ ca. 90°, was also applied. The crystal structure was solved by the heavy-atom approach. The systematically absent reflections: hkl when $h + k \neq 2n$ and $h0l$ when $l \neq 2n$, are compatible with two space groups, viz. Cc and $C2/c$. With only four formula units in the latter, dimeric molecules must either lie on a crystallographic center of symmetry or C_2 symmetry axis. Approximate coordinates for the As atoms, derived from a Patterson map, were related by a center of symmetry and thus all further calculations were performed using equivalent positions appropriate to the centrosymmetric space group $C2/c$. The remaining non-hydrogen atoms were located in a series of weighted F_o and difference Fourier syntheses. Positional and thermal parameters of the non-hydrogen atoms (at first isotropic, then anisotropic) were adjusted by means of several rounds of full-matrix least-squares calculations. In the later iterations, hydrogen atoms were incorporated at their calculated positions (C-H = 1.05 Å) and an extinction correction was included as a variable. A final difference Fourier synthesis contained no unusual features. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from reference 9.

DISCUSSION

Dehalosilylation reactions between a Group 13 halide and $\text{As}(\text{SiMe}_3)_3$ have been used to prepare dimeric and mixed bridge species, $\overline{\text{M-As-M-As}}$ and $\overline{\text{M-As-M-Cl}}$, respectively, where $\text{M} = \text{Ga}$ and In . It has been shown that in the case of indium halides, dimers may be prepared if reaction is carried out in a 1:1 mole ratio and mixed bridges if a 2:1 stoichiometry of In to As reagents is employed.⁵ However, no gallium-arsenic dimers have been isolated utilizing such reactions. Instead, only mixed bridge products have been obtained in reactions of either 1:1 or 2:1 stoichiometry of Ga to As reactants.^{4,6,7} While this method has been shown to be of general utility in these systems, seminal investigations show it to fail as group three is ascended to aluminum. Thus, reaction of Et_2AlCl with $\text{As}(\text{SiMe}_3)_3$ at ambient temperature in either 1:1 or 2:1 stoichiometry (eq 1) gives only **2** with no evidence of silyl cleavage.

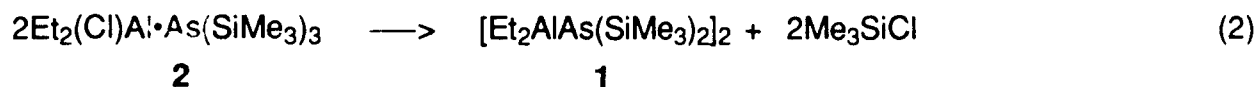


This behavior may be understood by consideration of the relative strengths of the Group 13-Cl bonds. They are 420.7, 354.0 and 328.0 kJmol^{-1} for Al , Ga and In , respectively.¹⁰ Since this bond is much stronger in the case of aluminum, its cleavage may be energetically unfavored and, hence, dehalosilylation is not observed. Instead, simple adducts are formed. To date, reaction conditions have not been varied to elucidate the effect of temperature upon such reactions. Such steps may provide a driving force that would enable dehalosilylation to occur.

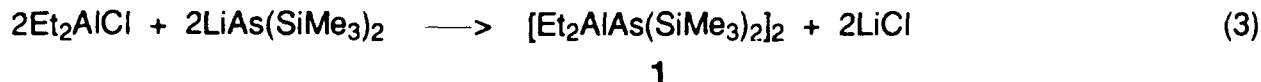
While crystals of **2** suitable for single crystal X-ray analysis have not been obtained, other data support the postulation of its structure as an adduct. Its ^1H ,

$^{13}\text{C}\{^1\text{H}\}$ and $^{27}\text{Al}\{^1\text{H}\}$ NMR spectra suggest such a formulation in that the ^1H integration and splitting patterns are compliant, the $^{13}\text{C}\{^1\text{H}\}$ spectrum intensities are appropriate for those peaks observed and only one type of aluminum is present as evidenced by a single peak in the $^{27}\text{Al}\{^1\text{H}\}$ spectrum. This, coupled with a partial elemental analysis (C, H and Cl), the fact that no Me_3SiCl was found in reaction volatiles and that yield was nearly quantitative, indicates that the structure of the product is correctly stated as **2**.

It was previously shown by us that the adduct $\text{Cl}_3\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$ undergoes intramolecular dehalosilylation to give AIAs when heated neat, under vacuum, in a cool flame.¹¹ With this in mind, attempted internal dehalosilylation of **2** was undertaken. Here, however, it was achieved at a much lower temperature. An NMR tube sample of **2** in benzene- d_6 was heated at 87°C for four days. ^1H NMR spectra taken as early as one day after heating showed peaks that may be attributed to compound **1** and Me_3SiCl . Thus, dehalosilylation may be brought about under very mild conditions in the case of **2** (eq 2).



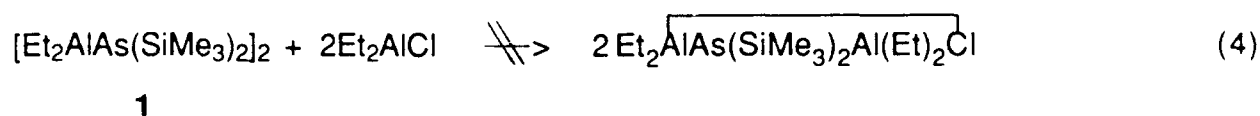
Compound **1** was prepared initially in relatively high yield (65%) by employing a coupling reaction between $\text{LiAs}(\text{SiMe}_3)_2$ and Et_2AlCl at -78°C (eq 3). When carried



out at room temperature, product was obtained in very low yield with an uncharacterized viscous, orange liquid as the predominant product. It is noteworthy

that, prior to this work, only four other arsinoalanes had ever been reported.¹²⁻¹⁵ Three of them are dimers^{12,14,15}, but only one was fully characterized by single crystal X-ray analysis¹⁶

The conversion of sundry Group 13-As dimers to mixed-bridge compounds by treatment with two mole equivalents of a dialkyl Group 13 halide has been shown to be applicable to such Ga and In containing species.^{5,16,17} However, it was found that this methodology was not successful for **1**. Upon treatment with two mole equivalents of Et₂AlCl, no reaction was observed (eq 4), as evidenced by ¹H and ¹³C NMR spectra.



This suggests that perhaps the dimer does not undergo dissociation in solution, thus not allowing for the monomeric unit to react with the aluminum halide.

Crystals of **1** suitable for X-ray analysis were grown from pentane. Crystallographic data are reported in Table I. An ORTEP diagram showing the atom numbering scheme is presented in Figure I. Table II lists the non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters while selected bond lengths and angles are given in Table III.

Compound **1** crystallizes in the monoclinic space group *C2/c* with the four discrete dimeric molecules in the unit cell lying on crystallographic centers of symmetry, and thus the $\overline{\text{Al-As-Al-As}}$ ring is constrained to be exactly planar as is the case for the only other previously characterized aluminum-arsenic dimer, [Et₂AlAs(*t*-Bu)₂]₂ (**3**).¹⁵ The mean Al-As distance of 2.535 Å in **1** is slightly shorter than that of 2.567 Å in **3**. The mean of the Al-C(1) [1.965(6) Å] and Al-C(3) [1.986(6) Å] bond distances at 1.976 Å in **1** is also slightly less than the corresponding mean of 1.992 Å in **3**. The geometry

about the Al and As atoms in **1** is distorted tetrahedral with the endocyclic angle subtended at As [Al-As-Al' = 91.01(5)°] being slightly larger than that at Al [As-Al-As' = 88.99(5)°]; the difference between the Al-As-Al' and As-Al-As' angles in **3** [94.54(4)° vs. 85.64(4)°] is much more pronounced. The Si-As-Si and C-Al-C angles at 107.59(6)° and 115.0(3)° in **1** deviate from tetrahedral in the same sense as do the C-As-C and C-Al-C angles, 108.9(3)° and 111.5(3)°, respectively, in **3**.

Compound **1** is of particular interest because it may be useful as a single-source precursor for the facile formation of AIAs. There are several ways in which this molecule may be envisaged as being utilized for such purposes. The ethyl groups provide for the possibility of β -hydrogen transfer with concurrent evolution of ethene and subsequent elimination of trimethylsilane to give AIAs. A second possibility is alcoholysis. Douglas and Theopold showed that a Ga-As dimer, when treated with methanol, underwent internal elimination to give GaAs.¹⁸ The third way in which AIAs might be obtained is to take advantage of the fact that covalent halides are known to cleave the silicon-arsenic bond.¹⁹ Thus, treatment of **1** with HCl should afford Me₃SiCl and an AsH₂-containing species which should readily eliminate ethane, or ethene and dihydrogen, to yield AIAs.

CONCLUSIONS

The work presented herein shows the viability of lithium chloride elimination reactions in the preparation of aluminum-arsenic dimers. While this methodology was successfully applied, dehalosilylation reactions were ineffective in that an aluminum-arsenic-chlorine mixed-bridge compound nor a dimer could be prepared directly by this route; albeit, evidence was obtained which indicated an adduct underwent dehalosilylation on heating to give a dimer. This study will be used as a starting point for further investigation of aluminum-arsenic systems. Through variation of temperature, substituents on aluminum and other reaction conditions a better

understanding of the limitations and applications of lithium halide elimination and dehalosilylation reactions to the preparation of single-source precursors to AIAs may be developed.

Acknowledgements. Financial support from the Office of Naval Research is greatly appreciated.

Supplementary Materials Available: Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, complete lists of interatomic distances and angles, including torsion angles for **1**, and equations of least-squares planes through groups of atoms (5 pages); a listing of observed and calculated structure amplitudes for **1** (14 pages). Ordering information is given on any current masthead page.

References

- (1) Cowley, A.H.; Jones, R.A. *Angew. Chem. Intl. Ed. Engl.* **1989**, *28*, 1208.
- (2) Cole-Hamilton, D.J. *Chem. in Brit.* **1991**, 852.
- (3) Purdy, A.P.; Wells, R.L.; McPhail, A.T.; Pitt, C.G. *Organometallics* **1987**, *6*, 2099.
- (4) Holley, W.K.; Pasterczyk, J.W.; Pitt, C.G.; Wells, R.L. *Heteroatom Chem.* **1990**, *1*, 475.
- (5) Wells, R.L.; Jones, L.J.; McPhail, A.T.; Alvanipour, A. *Organometallics*. **1991**, *10*, 2345.
- (6) Wells, R.L.; Purdy, A.P.; Higa, K.T.; McPhail, A.T.; Pitt, C.G. *J. Organomet. Chem.* **1987**, *325*, C7.
- (7) Wells, R.L.; Holley, W.K.; Shafieezad, S.; McPhail, A.T.; Pitt, C.G. *Phosphorus, Sulfur, Silicon and Related Elem.* **1989**, *41*, 15.
- (8) Becker, G.; Gutekunst, G.; Wessely, H.J., *Z. Anorg. Allg. Chem* **1980**, *462*, 113.
- (9) *International Tables for X-ray Crystallography*, The Kynoch Press, Birmingham, England, 1974, Vol IV.
- (10) Huheey, J.E. *Inorganic Chem. 3rd Ed.* Harper and Row Publishers, New York, NY, 1983.
- (11) Wells, R.L.; Pitt, C.G.; McPhail, A.T.; Purdy, A.P.; Shafieezad, S.; Hallock, R.B. *Mat. Res. Soc. Symp. Proc.* **1989**, *131*, 45.
- (12) Coates, G.E.; Graham, J. *J. Chem. Soc.* **1963**, 233.
- (13) Beachley, O.T.; Coates, G.E. *J. Chem. Soc.* **1965**, 3241.
- (14) Arif, A.M.; Benac, B.L.; Cowley, A.H.; Jones, R.A.; Kidd, K.B.; Nunn, C.M. *New J. Chem.* **1988**, *12*, 253.
- (15) Heaton, D.E.; Jones, R.A.; Kidd, K.B.; Cowley, A.H.; Nunn, C.M. *Polyhedron* **1988**, *7*, 1901.

- (16) Holley, W.K.; Wells, R.L.; Shafieezad, S.; McPhail, A.T.; Pitt, C.G. *J. Organomet. Chem.* **1990**, *381*, 15.
- (17) Wells, R.L.; Pasterczyk, J.W.; McPhail, A.T.; Johansen, J.D.; Alvanipour, A. *J. Organomet. Chem.* **1991**, *407*, 17.
- (18) Douglas, T.; Theopold, K.H. *Inorg. Chem.* **1991**, *30*, 596.
- (19) Abel, E.W.; Illingworth, S.M. *J. Chem. Soc. (A)* **1969**, 1094.

Caption to Figure

Figure 1. ORTEP diagram (40% probability ellipsoids) showing the solid-state conformation and atom numbering scheme of $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$ (1); primed atoms are related to unprimed atoms by a crystallographic center of symmetry. Hydrogen atoms have been omitted for clarity.

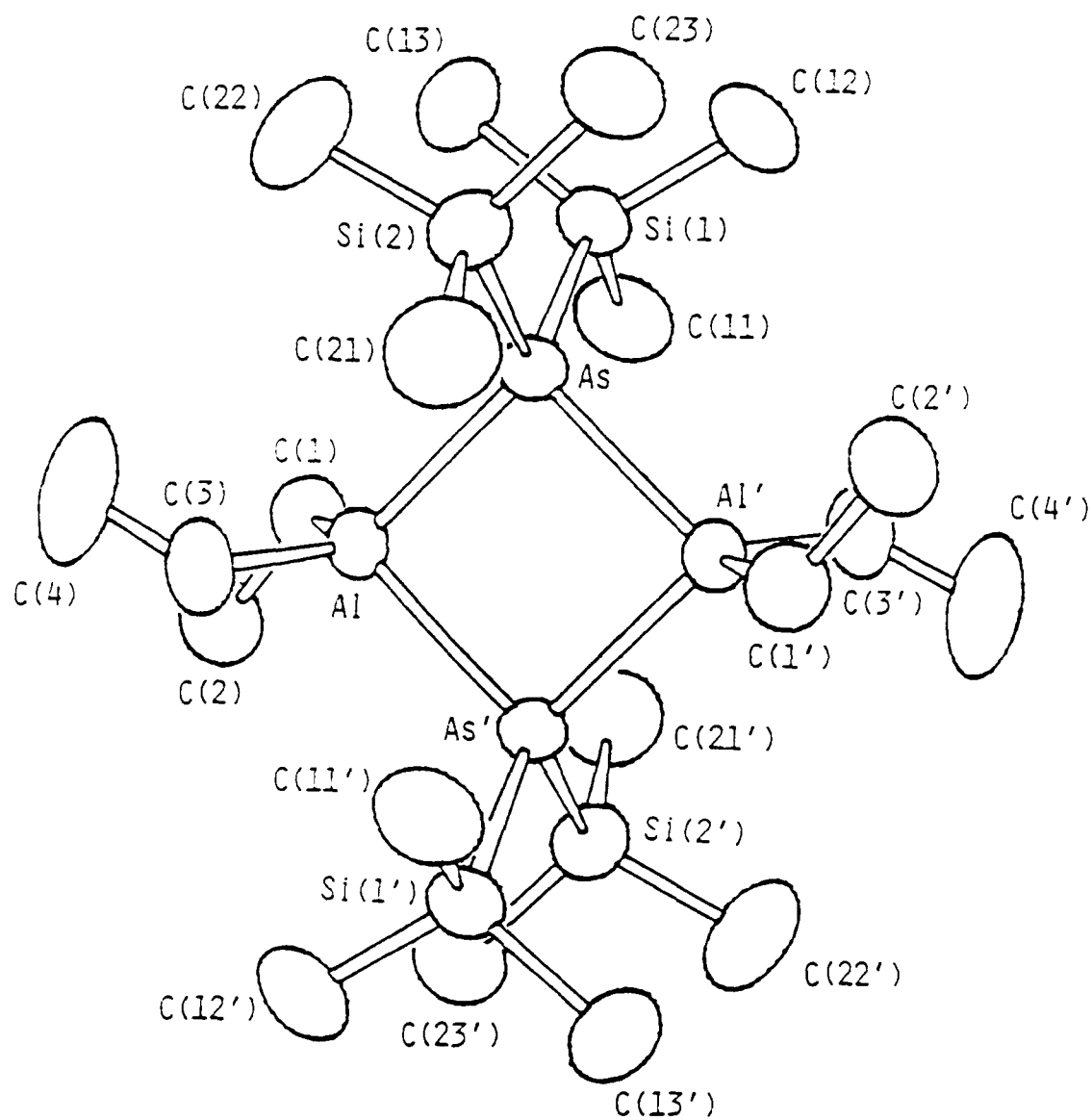


Table 1. Crystallographic Data^a for [Et₂AlAs(SiMe₃)₂]₂ (1)

Molecular formula	C ₂₀ H ₅₆ Al ₂ As ₂ Si ₄
Formula weight	612.82
Crystal system	monoclinic
Space group	C2/c(C _{2h} ⁶) - No.15
a(Å)	18.214(2)
b(Å)	9.542(1)
c(Å)	20.453(2)
β(°)	99.89(1)
No. of orientation refls.; θ(°) range	25; 40-45
V(Å ³)	3502(1)
Z	4
D _{calcd.} (g cm ⁻³)	1.162
μ(Cu-Kα radiation, λ = 1.5418 Å)	42.5
Temp. (°C)	23
Crystal dimensions (mm)	0.15 x 0.25 x 0.32
T _{max} :T _{min}	1.00:0.65
Scan type	ω-2θ
Scanwidth (°)	0.70 + 0.14tanθ
θ _{max} (°)	75
Intensity control refls.; variation; repeat time (hr)	3 1 2, 2 2 2, 1 3 $\bar{1}$, 2 2 $\bar{4}$; <2% ; 2
Total no. of refls. (+h,+k,±l) recorded	3705
No. of non-equiv. refls. recorded	3118
R _{merge} (on I)	0.023
No. of refls. retained [I > 3.0σ(I)]	1968
No. of parameters refined	128
Extinction correction	3.7(1) x 10 ⁻⁶
R(R _w) ^b	0.039 (0.053)
Goodness-of-fit ^c	1.11
Max. shift/esd in final least-squares cycle	0.02
Final Δρ(e/Å ³) max.;min.	0.32 ; -0.58

^aAn Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator was used for all measurements. Crystallographic calculations were performed on PDP11/4

Table 1. (Continued)

and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP).

$bR = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $R_w = [\Sigma \omega (|F_o| - |F_c|)^2 / \Sigma \omega |F_o|^2]^{1/2}$; $\Sigma \omega D^2$ [$\omega = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized.

$\chi^2_{\text{Goodness-of-fit}} = [\Sigma \omega \Delta^2 / (N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$.

Table II. Non-hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 1, with Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{eq}(\text{\AA}^2)$
As	0.18753(3)	0.25453(6)	-0.07961(2)	4.06(1)
Al	0.18075(7)	0.3337(2)	0.04040(7)	4.25(3)
Si(1)	0.10419(8)	0.0731(2)	-0.11613(7)	5.27(3)
Si(2)	0.17122(9)	0.4338(2)	-0.15669(7)	5.68(3)
C(1)	0.1045(3)	0.2321(6)	0.0788(3)	5.7(1)
C(2)	0.1042(4)	0.2663(7)	0.1520(3)	7.5(2)
C(3)	0.1774(3)	0.5409(6)	0.0486(3)	6.7(1)
C(4)	0.1042(4)	0.6022(8)	0.0471(5)	11.8(2)
C(11)	0.1094(4)	-0.0631(7)	-0.0520(3)	7.8(2)
C(12)	0.0072(3)	0.1409(8)	-0.1347(4)	9.4(2)
C(13)	0.1301(4)	-0.0092(8)	-0.1915(3)	8.2(2)
C(21)	0.0790(4)	0.5213(9)	-0.1594(4)	10.0(2)
C(22)	0.1754(4)	0.3628(9)	-0.2401(3)	8.3(2)
C(23)	0.2467(4)	0.5662(7)	-0.1334(4)	8.8(2)

**Table III. Selected Bond Distances (Å) and Angles (deg) for 1 with
Estimated Standard Deviations in Parentheses**

Bond Lengths

As-Al	2.539(2)	As-Si(1)	2.351(2)
As-Si(2)	2.347(2)	As-Al'	2.531(1)
Al-C(1)	1.965(6)	Al-C(3)	1.986(6)

Bond Angles

Al-As-Si(1)	114.10(6)	Al-As-Si(2)	114.79(6)
Al-As-Al'	91.01(5)	Si(1)-As-Si(2)	107.59(6)
Si(1)-As-Al'	112.30(6)	Si(2)-As-Al'	116.60(6)
As-Al-C(1)	112.5(2)	As-Al-C(3)	112.5(2)
As-Al-As'	88.99(5)	C(1)-Al-C(3)	115.0(3)
C(1)-Al-As'	114.7(2)	C(3)-Al-As'	110.3(2)

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, VA 22217-5000

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, DC 20375-5000

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Weapons Center
China Lake, CA 93555-6001

Dr. Eugene C. Fischer (1)
Code 2840
David Taylor Research Center
Annapolis, MD 21402-5067

Dr. Elek Lindner (1)
Naval Ocean Systems Center
Code 52
San Diego, CA 92152-5000

Commanding Officer (1)
Naval Weapons Support Center
Dr. Bernard E. Doua
Crane, IN 47522-5050

Dr. Richard W. Drisko (1)
Naval Civil Engineering Lab.
Code L52
Port Hueneme, CA 93043

Dr. Harold H. Singerman (1)
David Taylor Research Center
Code 283
Annapolis, MD 21402-5067

Chief of Naval Research (1)
Special Assistant for Marine
Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA 22217-5000

Defense Technical
Information Center (2)
Building 5, Cameron Station
Alexandria, VA 22314